PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvement in Separating Residual Gases of an Ammonia Synthesis Process

We, VEB LEUNA-WERKE "WALTER ULBRICHT", a Corporation organised and existing under the laws of Eastern Germany, of Leuna, near Merseburg, Eastern Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that the rare gases contained in the air, particularly argon, krypton, xenon, helium and neon, are obtained from the products occurring in the decomposition of air.

For the production of argon from the oxygen-nitrogen separating column, for example, a gas mixture is taken from the point at which there is the greatest concentration of argon. This gas mixture, of which the maximum argon content is 7%, the remainder consisting of nitrogen and oxygen, is subjected to a two stage distillation process, in which the argon is obtained with a purity of about 98%. The use of the resulting product as welding argon involves difficulties due to the presence of the oxygen. Further concentration, to the point where a welding quality is obtained, can only be effected by means of a subsequent fine purification process. The expense involved in the production of an argon for welding purposes by this process is thus considerable.

For the production of krypton and xenon, oxygen is tapped off at that point of the air decomposition apparatus at which the maximum possible crypton-xenon concentration, governed by the technology of oxygen production, is present. In large scale oxygen plant this is generally the liquid oxygen in the acetylene separator. In this process, the magnitude of the concentration deliberately brought about and the yield of crypton and xenon depend on the simultaneous enrichment of the hydrocarbons in the liquid oxygen. The quantity of enriched hydrocarbons must be as far as possible below the solubility limit of hydrocarbons, particularly acetylene, in the liquid oxygen. The process described in the foregoing for krypton-xenon production, is current industrial practice.

A process for producing rare gases from the residual ammonia gases of an ammonia synthesis process is also known, in which the expansion gas of the ammonia synthesis is subjected under pressure, to a water washing process and to drying with silica gel, after which the gas mixture is cooled in heat exchangers connected to the apparatus in series, partially liquefied and, after expansion through a throttle orifice, introduced into a separating apparatus in order to further enrich the rare gases. In this operation the necessary cooling is provided by an auxiliary refrigeration circuit based on nitrogen, a so called Heylandt circuit. This process is more economical and far less dangerous than those described above, as it is not carried out with oxygen or consequently with hydrocarbons in oxygen. It also enables rare gases to be obtained with a considerable degree of purity. However, in this process also, a high input of energy is also involved.

It has now been found that rare gases and other products of distillation can be obtained from residual gases of an ammonia synthesis process, and preferably in the liquid phase or in the gaseous and liquid phase, and with a considerable degree of purity, in a particularly economical manner, i.e. with fairly complete utilisation of the potential energy available, if the residual gases of the synthesis plant are conveyed under pressure to a low temperature decomposition apparatus

[*Price 4s. 6d.*]

after they have been freed of constituents which have a high boiling point and/or sublimate easily, and if they are expanded in the said apparatus, the expansion process being accompanied at least to some extent by the performance of work, and if they are then conveyed wholly or partially liquefied, to the separating columns for the separation by the distillation process of the rare gases and/or other products of distillation, and if the thermal economy of the low temperature decomposition apparatus is compensated by the operation of a suitably arranged auxiliary refrigeration circuit.

In this process it is of advantage to expand one or more products of the low temperature decomposition apparatus in order to compensate the thermal economy of the said apparatus still further, the expansion being accompanied by the performance of work.

It is also found desirable to connect the auxiliary refrigeration circuit with one or more products of the low temperature decomposition apparatus.

The accompanying drawing shows diagrammatically a constructional example of a plant for carrying out the process according to the invention. As shown, the plant consists of a heat exchanger 1 to which the synthesis gas to be decomposed is conveyed, as crude gas, through a pipe 2, and of an expansion machine 3 in which the crude gas or a part thereof is expanded, the expansion being accompanied by the performance of work, while for the gas to be expanded without the performance of work, a throttle type expansion device 4 is provided in parallel with the expansion machine. A heat exchanger 5 is also provided, in which the crude gas undergoing expansion at least partly accompanied by the performance of work, is partially liquefied. A pipe 7 is provided to enable the crude gas thus treated to be conveyed to a separating apparatus 6. The separating apparatus 6 is equipped with an outlet pipe 8 through which the hydrogen produced under pressure is conveyed to the heat exchanger 5. The hydrogen is conveyed through a pipe 9 to an expansion machine 10 to which is connected a pipe 11, through which the hydrogen emerges from the plant via the heat exchanger 5, a pipe 12 and the heat exchanger 1. The separating apparatus 6 has further outlet pipes 13, 14 and 15, through which the constituents produced in the separating apparatus 6 in the course of the decomposition of the crude gas are extracted. While a product in liquid form can be withdrawn through the pipe 15, the pipes 13 and 14 are connected, via the heat exchanger 5 and the pipes 16 and 17, with the heat exchanger 1, in order to remove products from the plant in the form of gases. Finally, the separating apparatus 6 has a further outlet pipe 18 which connects the said plant with the krypton separating apparatus 19. The krypton separating apparatus 19 has two outlet pipes 20 and 21 for liquid products, while a pipe 22 leads to a heat exchanger 23 and passes via the pipe 24 and the heat exchanger 25, in order to enable a further product to be withdrawn from the plant in the form of gas. The heat exchangers 23 and 25 form a part of an auxiliary refrigeration circuit which is provided in order to enable the cooling efficiency of the separating apparatus 6 to be maintained. Within the pipe of this auxiliary refrigeration is a throttle 26 through which the super-cooled re-cycle medium is expanded, so that it enters in a liquid state into the separating apparatus 6. The outlet pipe through which the re-cycle medium evaporated in the separating apparatus 6 is conveyed to the heat exchanger 27 is given the reference number 28. The connecting pipe through which the re-cycle medium evaporated is conveyed into the heat exchanger 23 has the reference number 29, while the connecting pipe for the re-cycle medium evaporated, between the heat exchangers 23 and 25, is numbered 30. The re-cycle medium is conveyed through the pipe 31 to a compressor 32. The pipes 33, 34 and 35 convey the compressed re-cycle medium, via the heat exchangers 25, 23 and 27, in which it is cooled down, liquefied and super-cooled, to the throttle in the pipe 26. An extraction pipe 36 between the heat exchangers 25 and 23 on the pipe 34, leads to the expansion machine 37 in which some of the re-cycle medium compressed in the compressor 32 and cooled in the heat exchanger 25 is expanded, the expansion being accompanied by the performance of work, and fed into the pipe 29 via the pipe 38.

EXAMPLE 1:—

In the low temperature decomposition plant described, krypton and xenon in a liquid state, pure argon to the extent of 50% in the gaseous state with a temperature of +10° C and 50% in the liquid state, methane to the extent of 80% in the gaseous state with a temperature of +10° C and 20% in the liquid state, and nitrogen and hydrogen in a gaseous state and likewise with a temperature of +10° C, are to be produced from a crude gas which consists of 50% hydrogen, 20% nitrogen, 15% argon and 15% methane and which contains traces of krypton and xenon.

For this purpose, 1000 Nm^3 (cubic metres at N.T.P.) of crude gas, consisting of 500 Nm^3 of hydrogen, 200 Nm^3 of nitrogen and 150 Nm^3 of argon, 150 Nm^3 of methane, and having traces of krypton and xenon, is conveyed through the pipe 2 at a pressure of 200 atm. and a temperature of +20° C, into the heat exchanger 1 where it is cooled down

to $-30°$ C. In the expansion machine 3, 800 Nm^3 of the crude gas is expanded to a pressure of 10 atm the expansion being accompanied by the performance of work, while the remaining 200 Nm^3 is expanded in the throttle 4 and by-passes the expansion machine. In this operation the crude gas cools down to a mixed temperature of $-100°$ C, and after partial liquefaction in the heat exchanger 5 is is conveyed through the pipe 7 into the separating apparatus 6. Here it is separated into the hydrogen fraction, nitrogen and argon fraction and a methane fraction containing krypton and xenon.

The "hydrogen" fraction, consisting of 500 Nm^3 of hydrogen and 100 Nm^3 of nitrogen, emerges from the separating apparatus 6 via the pipe 8 at a pressure of 10 atm and at a temperature of $-192°$ C, and heats up in the heat exchanger 5 to $-130°$ C. Through the pipe 9 this fraction is conveyed into the expansion machine 10, where it is expanded to 1.1 atm. At the temperature of $-185°$ C which sets in during the expansion it is conveyed through the pipe 11, via the heat exchanger 5 and through the pipe 12 into the heat exchanger 1, and is drawn out of the plant at a temperature of $+10°$ C for further use.

The "nitrogen" fraction, consisting of 100 Nm^3 of nitrogen and 20 Nm^3 of argon, is conveyed at a temperature of $-180°$ C and a pressure of 1.3 atm. and via the pipe 13 to the heat exchanger 5, and also via the pipe 16 to the heat exchanger 1, leaving the plant at a temperature of $+10°$ C.

The argon fraction consists of 130 Nm^3 of argon. 65 Nm^3 of this fraction leaves the plant as gas via the pipe 14 and the heat exchanger 5, after passing through the pipe 17 and the heat exchanger 1, the gas having a temperature of $+10°$ C and a pressure of 1.3 atm. The remaining 65 Nm^3 of this fraction is withdrawn in the liquid phase via the pipe 15, to be put to further use.

The methane fraction consisting of 150 Nm^3 of methane and 0.015 Nm^3 of krypton and xenon, is conveyed to the krypton separating apparatus 19 through the pipe 18. Here 0.015 Nm^3 of krypton xenon mixture is separated, leaving as liquid from the krypton separating apparatus 19 via the pipe 20. 30 Nm^3 of liquid methane is withdrawn from the plant via the pipe 21, to be put to further use. 120 Nm^3 of liquid methane is withdrawn at a pressure of 1.3 atm from the krypton separating apparatus 19 via the pipe 22, and conveyed to the heat exchanger 23 of the auxiliary nitrogen-based refrigerating circuit. In the heat exchanger 23 the methane is evaporated, and to cause it to give off its perceptible heat, it is conveyed through the pipe 24 to the heat exchanger 25. Here it leaves the plant at a temperature of $+10°$ C for further use. 500 Nm^3 of nitrogen at a pressure of 50 atm is conveyed in counterflow to the methane through the pipe 33, and via the heat exchanger 25 and the pipe 34 into the heat exchanger 23, where it is liquefied by the said methane, after which it is conveyed through the pipe 35 into the heat exchanger 27, where it is supercooled and conveyed as liquid re-cycle nitrogen and after expansion to 1.5 atm in the throttle device 26, to the separating apparatus 6. This nitrogen serves to maintain the heat balance of the separating apparatus. The 500 Nm^3 of nitrogen evaporated in the separating apparatus 6 is conveyed through the pipe 28 and at a temperature of $-193°$ C to the heat exchanger 27 and through the pipes 29 and 30 to the heat exhangers 23 and 25 to enable it to give off its perceptible heat. It leaves the separating apparatus through the pipe 31 and at a temperature of $+10°$ C and a pressure of 1.1 atm and is re-compressed to 50 atm. in a circulating compressor 32.

EXAMPLE 2:—

In the same low temperature decomposition plant, and from the same crude gas, liquid products krypton-xenon and argon and 80% methane and gaseous products hydrogen, nitrogen and 20% methane are to be obtained, at a temperature of $+10°$ C. For this purpose, 1000 Nm^3 of crude gas consisting of 500 Nm^3 of hydrogen, 200 Nm^3 of nitrogen, 150 Nm^3 of argon and 150 Nm^3 of methane, and having traces of krypton and xenon, are conveyed into the heat exchanger 1 through the pipe 2, and at a pressure of 200 atm and a temperature of $+20°$ C, where they are cooled down to $-30°$ C, and are expanded to 10 atm in the expansion machine 3. In this process the crude gas cools down to $-120°$ C, and after partial liquefaction in the heat exchanger 5 it is conveyed through the pipe 7 into the separating apparatus 6. Here the separation into the fractions hydrogen, nitrogen and argon, and a methane containing krypton and xenon, is carried out.

The hydrogen fraction consisting of 500 Nm^3 of hydrogen and 100 Um^3 of nitrogen, leaves from the separating apparatus 6 via pipe 8 under a pressure of 10 atm and at a temperature of $-192°$ C, and heats up to $-150°$ C in the heat exchanger 5. This fraction is conveyed through the pipe 9 into the expansion machine 10, where it is expanded to 1.1 atm. It is conveyed at a temperature of $-200°$ C through the pipe 11, via the heat exchanger 5 and through the pipe 12, into the heat exchanger 1, and it leaves at a temperature of $+10°$ C therefrom for further utilisation.

The nitrogen fraction, consisting of 100 Nm^3 of nitrogen and 20 Nm^3 of argon, is conveyed at a temperature of $-180°$ C and a pressure of 1.3 atm via the pipe 13 to the

heat exchanger 5, and via the pipe 16 to the heat exchanger 1, leaving the exchanger at a temperature of +10° C.

The argon fraction, consisting of 130 Nm^3 of argon, is withdrawn from the separating apparatus 6 in liquid phase and via the pipe 15, to be further utilised. The methane fraction, consisting of 150 Nm^3 of methane and 0.015 Nm^3 of krypton and xenon, is conveyed through the pipe 18 to the krypton separating apparatus 19. Here the 0.015 Nm^3 of krypton and xenon are separated, leaving in the liquid phase via the pipe 20. 120 Nm^3 of liquid methane is withdrawn at a pressure of 1.3 atm and via the pipe 21, from the krypton separating plant 19. 30 Nm^3 of methane is conveyed via the pipe 22 and the heat exchanger 23, as well as via the pipe 24 and the heat exchanger 25, to the auxiliary refrigeration circuit based on nitrogen, and leaves the plant after giving off the heat of evaporation and the perceptible heat. To equalise the heat balance, the auxiliary refrigeration circuit is assisted by a nitrogen operated expansion machine 37. For this purpose, 1800 Nm^3 of nitrogen, in a counterflow to the 30 Nm^3 of methane, is conveyed at a pressure of 50 atm through the pipe 33 into the heat exchanger 25. This process is accompanied by the cooling of the nitrogen to −90° C. 800 Nm^3 of nitrogen is conveyed through the pipe 34 into the heat exchanger 23, while 1000 Nm^3, after passing through the pipe 36, is expanded in the expansion machine 37, the latter step being accompanied by the performance of work. After the expansion, in which cooling to −170° C takes place, the nitrogen is introduced into the pipe 29 via the pipe 38. The 800 Nm^3 of nitrogen conveyed into the heat exchanger 23 via the pipe 34 is liquefied in the said exchanger, after which it is conveyed through the pipe 35 to the heat exchanger 27 where it is super-cooled, whereupon it is expanded to 1.5 atm in the throttle device in the pipe 26 and conveyed to the separating apparatus, as liquid re-cycle nitrogen in order to maintain the heat balance. The 800 Nm^3 of nitrogen evaporated in the separating apparatus is conveyed, via the pipe 28 and at a temperature of −193° C, to the heat exchanger 27, and via the pipes 29 and 30 to the heat exchangers 23 and 25, to enable the perceptible heat to be given off. This nitrogen emerges from the separating apparatus via the pipe 31, at a temperature of +10° C and a pressure of 1.1 atm and is re-compressed to 50 atm in a circulating compressor 32.

WHAT WE CLAIM IS:—

1. Method of producing rare gases and other distillation products from residual gases of an ammonia synthesis process, preferably in the liquid phase or in the gaseous and liquid phase, by means of low temperature distillation after the residual gases have been freed, under pressure, of constituents having a high boiling point and/or sublimating easily, which method comprises the steps of expanding the said residual gases in a low temperature decomposition plant, this being accompanied at least to some extent by the performance of work, and conveying gases in a wholly or partially liquefied state to separating columns for the separation by a distillation process of the rare gases and/or other distillation products, and in compensating the thermal economy of the low temperature decomposition plant by suitably arranged auxiliary refrigeration circuit.

2. Method in accordance with Claim 1, in which the thermal economy of the low temperature decomposition plant is further compensated by the expansion, accompanied by the performance of work, of one or more products of the low temperature decomposition plant.

3. Method in accordance with Claims 1 or 2, in which the auxiliary refrigeration circuit is connected to one or more products of the low temperature decomposition plant.

4. Method of and apparatus for the production of rare gases and other distillation products from residual gases of a synthesis process, substantially as herein described with reference to the accompanying drawing.

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1 SHEET

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